1 Hydrate a 3-D microstructure

The NIST cement hydration model operates directly on 3-D images of cement paste microstructure, such as those commonly generated using VCCTL software under the **Build Microstructure** submenu. Execution of the hydration model requires a starting microstructure, information about the curing conditions, knowledge of the availability or absence of excess water, and specifications of the frequency with which properties will be calculated and written to data files during the course of hydration. Clicking on this submenu entry generates a sequence of web forms, the first of which is shown in Figure 1, that guide the user in specifying all of this information so that a simulation of hydration can be properly launched.

1.1 Step 1: Starting microstructure

This form contains only two fields, as shown in Figure 1:

1.1.1 Random number seed

The user must enter a *negative integer* (in the range [-32767,-1]) in this field.

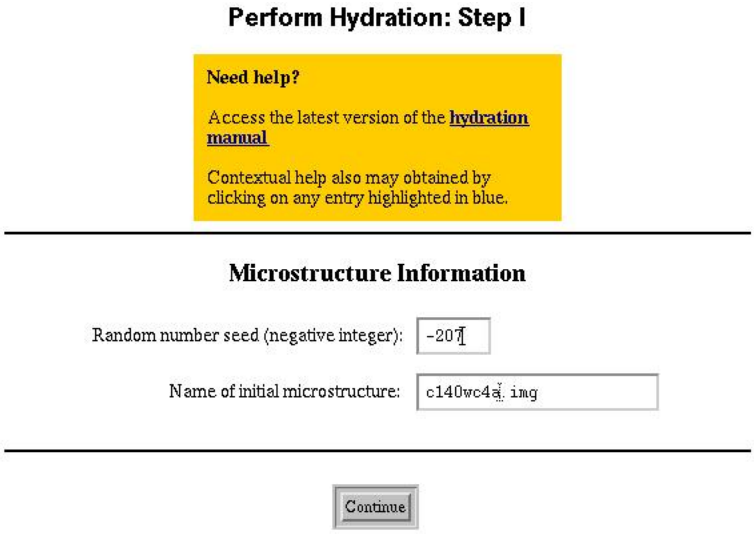

Figure 1: First of five forms for launching the VCCTL hydration model.

1.1.2 Name of initial microstructure

This should be the name of a valid microstructure image file (extension `.img`) and commonly will be one that has already had the four major clinker phases distributed (see **Distribute Cement Phases** submenu for more information). The web interface programs use this information, not only to supply the model with the file name, but also to construct the name of the corresponding *particle* image file and the `.info` file that contains information on the phase fractions and calculated numbers of one-pixel particles from the particle size distribution (PSD).

1.2 Step 2: Other microstructure information

This form, shown in Figures 2 and 4, appears after submitting the previous form by pressing its "Continue" button. It collects information about the number of one-pixel particles to place in the microstructure prior to hydration, and also about the volume fraction of aggregate if one is simulating hydration of the cement paste within concrete.

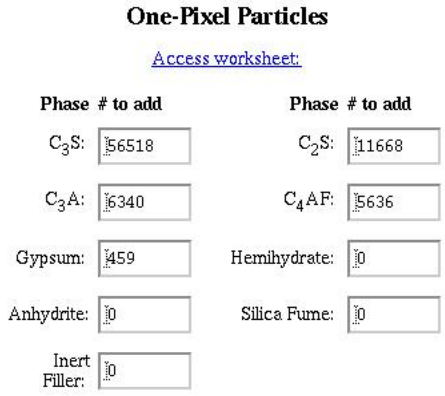

Figure 2: Top portion of the second of five forms for launching the VCCTL hydration model.

Version 1.0 file detected This message appears only if the name of the original microstructure file, entered in the previous form, appears *not* to have been created using VCCTL Version 1.1. In this case, Version 1.1 does not have access to several items of information, such as the particle image file, the number of one-pixel particles, etc. used during creation of the original file.

When a Version 1.0 file is detected here, the user is prompted for the name of the **particle** image file that was generated during creation of the original file. Unless the user has intentionally changed the naming convention in some way, the particle image file will have the same name as the original microstructure file, entered on the previous form, except that the character "p" is added at the beginning. This is the default name provided in this field. With a valid particle image file name, and an automatic scan of the original microstructure file, the software should be able to convert the file to Version 1.1 format.

NOTE: Version 1.1 *cannot* determine the numbers and types of one-pixel particles that should be added to microstructure that was created using Version 1.0. Therefore, when submitting a request for hydration of such a microstructure, the user will need to calculate the numbers and types of one-pixel particles using the online worksheet that is accessible from the hydration form (see the below for a description).

1.2.1 One-pixel particles

In previous versions of VCCTL, the determination of the correct number of one-pixel particles involved tedious calculation based on the individual PSDs and volume fractions of the anhydrous phases. In Version 1.1, however, much of this information is "remembered" and automatically uploaded to the form if the microstructure was created in the usual way described earlier in this

User's Guide. Therefore, under normal circumstances, the user will not need to adjust the values that are displayed on the form. Of course, the user is free to change the values at his/her discretion.

If the starting microstructure was created using any VCCTL version prior to 1.1, then the user must calculate the numbers of one-pixel particles. As an aid in this calculation, a worksheet is provided (see Figure 3). The worksheet will calculate the number of one-pixel particles of each of the four major clinker phases, as well as the various forms of calcium sulfate, based on the current number of pixels and targeted volume fractions of each of these phases in the microstructure. The current number of pixels of each phase may be obtained from the **Phase statistics** submenu. This form was also available in Version 1.0, but in Version 1.1 it has the additional feature that the data can be transferred directly from the completed worksheet to the form by pressing the "Update" button on the worksheet.

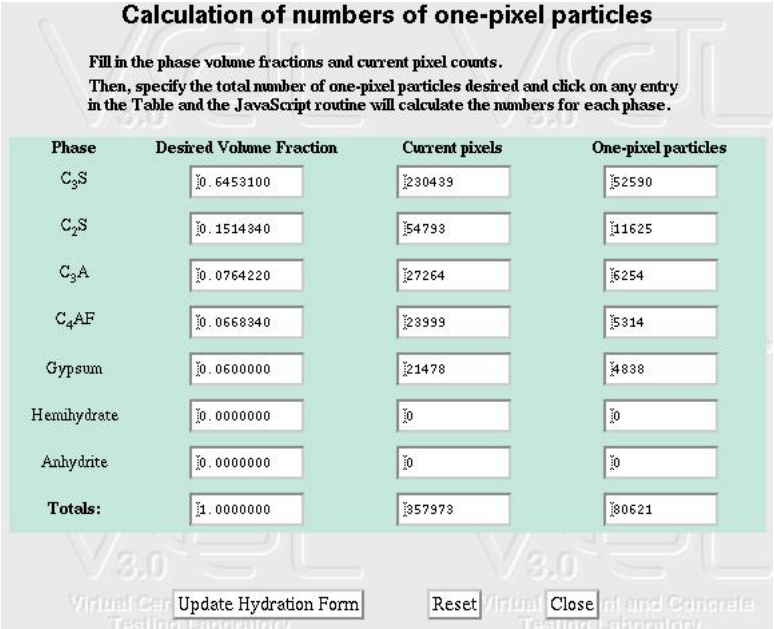

Figure 3: Supplemental worksheet for calculating the numbers of one-pixel particles of each major cement phase to be placed prior to hydration.

1.2.2 Other one-pixel particles

One-pixel particles of any phase recognized by the hydration model can be added to the microstructure prior to hydration. To add them, the user simply enters the phase identification for the desired phase and the number of one-pixel particles of that phase that are desired (see Figure 4). If the phase identification number of a particular compound is not known, clicking on the Phase ID link will display the list of all available phases and their corresponding integer identification numbers. Up to two additional phases can be specified in this way.

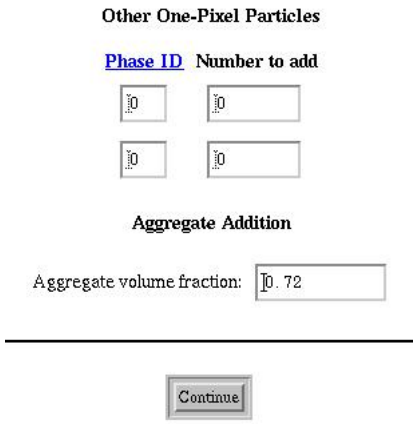

Figure 4: Bottom portion of the second of five forms for launching the VCCTL hydration model.

1.3 Step 3: Curing and kinetics

This is the third form in the sequence of five, and appears upon clicking the "Continue" button at the bottom of the previous form. The top portion of the form is shown in Figure 5. This form collects information about the time of hydration, specifications about the thermal conditions and availability of excess water, and data on the average apparent activation energies of the major hydration reactions.

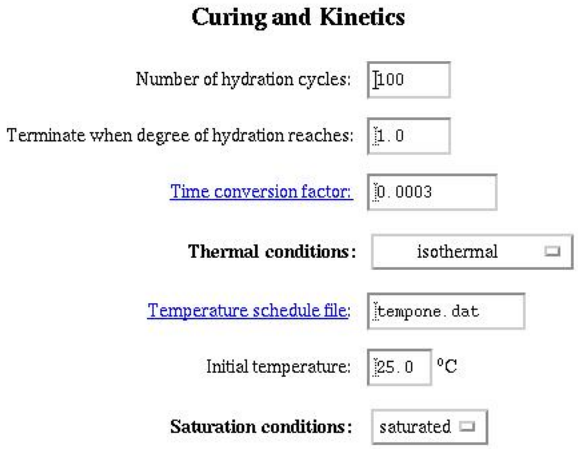

Figure 5: Top portion of the third of five forms for launching the VCCTL hydration model.

1.3.1 Number of hydration cycles

The hydration model operates by a sequence of steps: dissolution (in which solid pixels may detach from the solid to become mobile agents in the pore solution), random-walker diffusion of the mobile agents, and (possible) reaction between colliding pixels. One complete sequence of these steps is called a *cycle*. Although cement pastes of different composition and w/c ratio will produce different results, a typical Type I ordinary Portland cement with w/c = 0.40 will often set at ≈100 cycles (the default value on the form), and the capillary pore space will become disconnected at ≈500

cycles. Furthermore, Figure 6 shows the relationship between degree of hydration, α, and number of cycles for CCRL Cement 140 with w/c = 0.40.

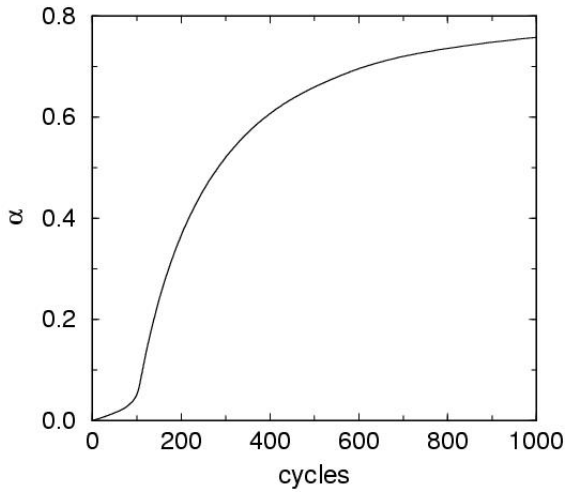

Figure 6: Plot of degree of hydration (α) versus number of hydration cycles for CCRL Cement 140 having w/c = 0.40. Curing was simulated at 25 °C under saturated conditions.

1.3.2 Terminate when degree of hydration reaches

This entry is optional. If the user would like the hydration to terminate as soon as a particular value of the degree of hydration (mass basis) has been achieved, that value may be entered here. The simulation will terminate when either this degree of hydration has been achieved, *or* when the specified number of hydration cycles has been executed, whichever happens first. By specifying 1.0 (the default value on the form) the simulation will execute for the number of cycles specified in the previous entry.

1.3.3 Time conversion factor

Hydration cycles have no intrinsic time scale. In the current version of VCCTL, hydration time t is related to the number of cycles n by the empirical relation

$$t = \beta n^2 \tag{1}$$

where β is the *time conversion factor* that is requested in this form entry. β has units of reciprocal time, and typical values for β are $\approx$0.0003 h^{-1} (the default value on the form) for a normal Type I Portland cement, and $\approx$0.0005 h^{-1} for a low-alkali cement.

It should be noted that the transformation in Eq. (1) is employed not for any fundamental reason, but rather because it often provides a reasonable fit to experimental measurements of α vs. t. A loose physical justification of the parabolic form of Eq. (1) is that diffusion through semipermeable hydration product, which obeys parabolic kinetics, becomes increasingly rate-controlling as hydration proceeds.

1.3.4 Thermal conditions

The next several form entries relate to the thermal conditions employed throughout curing. The first one involves choosing the thermal boundary conditions on the system, and the options are

1. **Isothermal**, for which it is assumed that the system is in diathermal contact with a constant-temperature reservoir and that heat transfer is sufficiently rapid to ensure that the system maintains the same constant temperature as the reservoir.
2. **Adiabatic**, for which it is assumed that the system is thermally isolated from its surroundings.
3. **Temperature-defined**, for which a pre-programmed temperature schedule is assumed to control the temperature of the system. See the **Specify a temperature schedule** submenu for information on creating a temperature schedule for use with this option.

1.3.5 Temperature schedule file

A valid temperature schedule file must be entered in this field *only* if the user chooses to use "temperature-defined" thermal conditions in the previous selection. Under isothermal or adiabatic/semi-adiabatic conditions, this field will not be used whether or not it contains a valid file name.

1.3.6 Initial temperature

The initial temperature is the starting temperature of the cement paste system. If hydration is being executed under a controlled temperature schedule, then the initial temperature of the temperature schedule overrides any value entered in this field.

1.3.7 Saturation conditions

The user has two options from which to choose:

1. **saturated**, for which the cement paste is assumed to be in contact with a reservoir of excess water. As free water in the capillary pore space is consumed by the hydration process, it is immediately replaced by water from the reservoir. Note, however, that once the capillary porosity reaches its percolation threshold and becomes disconnected, water replacement is no longer possible.
2. **sealed**, for which free water consumed during hydration is not replaced. Instead, the capillary pore space is progressively emptied of its water, starting in those pore regions with the largest effective diameters.

The bottom portion of the third form is shown in Figure 7. The form fields in this portion of the form relate to apparent activation energies of the main reactions that occur during hydration.

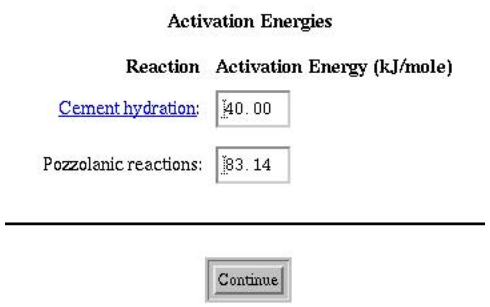

Figure 7: Bottom portion of the third of five forms for launching the VCCTL hydration model.

1.3.8 Cement hydration

For the present purposes, the process of cement hydration is considered as a single composite reaction with a characteristic apparent activation energy which could be measured in principle by making an Arrhenius plot of the rate of consumption of anhydrous phases vs. $1/T$. For a Type I cement, if no further information is available, ASTM C 1074 [1] suggests a value of 40 kJ/mol.

1.3.9 Pozzolanic reactions

The dissolution of portlandite (CH) due to pozzolanic influence is assumed to be a thermally activated process, and the activation energy entered here is used to calculate the intrinsic rate constant, k, for dissolution as a function of temperature according to an Arrhenius expression

$$k = k_0 \exp\left(\frac{-E_a}{RT}\right) \tag{2}$$

where k_0 is the reaction rate constant extrapolated to temperature $T = 0$, E_a is the activation energy requested here, in units of kJ/mol, and R is the gas constant in units of kJ/(mol·K).

The activation energy entered here for pozzolanic reactions is also assumed to influence the dissolution rate of fly ash phases (ASG and CAS_2). The default value is 100× the magnitude of the ideal gas constant, and may be used in the absence of additional information.

1.4 Step 4: Hydration behavior options

This form, shown in Figure 8, collects information on various aspects of the hydration process that have not been addressed previously.

1.4.1 Conversion of primary C–S–H to pozzolanic C–S–H

When silica fume or other pozzolans (fly ash, etc.) are present in the starting microstructure, the user may either allow or prohibit the conversion of primary C–S–H hydration product to pozzolanic C–S–H. Pozzolanic C–S–H has a lower Ca/Si ratio (which causes extra CH is to form when the primary C–S–H converts to the pozzolanic form) and a different molar volume from that of the

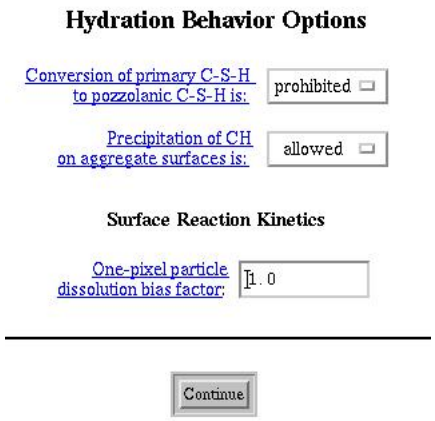

Figure 8: Fourth of five forms for launching the VCCTL hydration model (top portion).

primary C–S–H. The default condition is to prohibit the conversion of primary C–S–H. Please refer to the CEMHYD3D User's Manual [2] for more information.

1.4.2 Precipitation of CH on aggregate surfaces

If the microstructure contains an aggregate slab (see **Generate Initial Microstructure** submenu) the user may allow CH to precipitate directly on its surfaces. This will tend to significantly increase the CH volume fraction immediately adjacent to the aggregate surface, and will consequently decrease the capillary porosity in this region. Because this specific aspect of the interfacial transition zone (ITZ) microstructure is still somewhat controversial, the user has the option of activating this precipitation or prohibiting it (the default being to allow the precipitation). Please consult Refs. [3, 4] for additional information.

1.4.3 One-pixel particle dissolution bias

The probability of dissolution of one-pixel particles, regardless of their phase, can be increased using this parameter. It may be sensible to increase the bias if in the initial microstructure there are a substantial number of particles with diameters smaller than the system resolution. All such particles are assigned a diameter equal to the system resolution, so their higher reactivities will not be captured unless the bias is increased. Allowed values are in the range from 1.0 (no bias) to 100.

1.5 Step 5: Data output

This form, shown in Figure 9, is used to specify how frequently (in cycles) certain properties are evaluated and written to data files.

1.5.1 Evaluate percolation of porosity ...

Percolation properties like this one tend to be time consuming because they involve nested iterations over most or all of the system pixels. Therefore, it is recommended that percolation properties not be evaluated every cycle. The default value of 5 is large enough that performance is not significantly affected and yet low enough that percolation thresholds can still be resolved in the data.

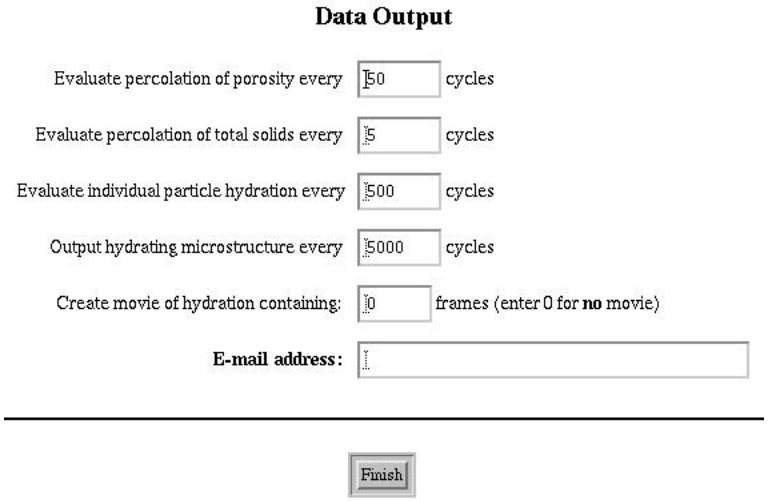

Figure 9: Fifth of five forms for launching the VCCTL hydration model.

1.5.2 Evaluate percolation of total solids ...

See the discussion in the previous subsection.

1.5.3 Evaluate individual particle hydration ...

The hydration model can keep track of the fraction of anhydrous phase reacted for each particle in the microstructure.

1.5.4 Output hydrating microstructure ...

The exact state of the entire microstructure can be saved at regular intervals during the hydration process. Although this can be helpful in preserving all the information about the course of microstructure development, keep in mind that each stored file requires between 1 and 8 Mb of storage.

1.5.5 Create movie of hydration ...

A positive integer n entered here will cause a 2-D slice of the microstructure to be stored in a file, such that n frames are created by the end of the simulation. The hydration model then

automatically creates an animated GIF file that can be viewed afterward. Consult the **View Animated Scan ...** submenu for details on viewing.

1.5.6 E-mail address

The program `disrealnew` that performs hydration may take anywhere from several minutes to several hours The actual time to completion depends on the number of cycles requested, the speed of the processor, and also depends on the size (total number of pixels) of the starting microstructure image. The VCCTL will automatically send a note to the e-mail address provided when execution completes. If no e-mail address is supplied, then a note will not be generated.

NOTE: The VCCTL is set up to perform up to two hydration simulations concurrently. Therefore, if the system is busy with two concurrent hydration simulations when another request is submitted, the user will be notified to resubmit the request at a later time.

1.6 Description of output file names and their contents

During hydration, several output files are created automatically. All of these files are named according to the convention:

```
fileroot.[...].N.T0.abc
```

where `fileroot` is the name of the initial microstructure file without the `.img` extension, `N` is the total number of hydration cycles, `T0` is the initial temperature, and the remaining flags `a`, `b`, and `c` take on the following values:

$$\texttt{a} = \begin{cases} 0 & \text{if C–S–H conversion is prohibited,} \\ 1 & \text{if C–S–H conversion is allowed} \end{cases}$$

$$\texttt{b} = \begin{cases} 0 & \text{under isothermal conditions,} \\ 1 & \text{under adiabatic conditions,} \\ 2 & \text{under temperature-defined conditions,} \end{cases}$$

$$\texttt{c} = \begin{cases} 0 & \text{under saturated curing,} \\ 1 & \text{under sealed curing} \end{cases}$$

The string [...] represents the data that are stored in the file, and may have any of the following values

`img` – microstructure image file after the hydration

`heat` – degree of hydration (both volume and mass bases), heat released, and gel-space ratio [5], all as a function of time

`adi` – system temperature as a function of time

`chs` – chemical shrinkage as a function of time

`pha` – phase volumes, in pixels, as a function of time

`pps` – results for the examination of the percolation of the water-filled capillary porosity vs. cycles, hydration time, and degree of hydration

`pts` – results for the examination of the percolation of the total solids vs. cycles, computed hydration time, and degree of hydration

`phr` – results for the hydration degree of individual particles after specific numbers of hydration cycles

When the final hydration form is submitted, all of the user input parameters are echoed back in a form, along with the names of all of the output files that may be created by the CEMHYD3D program. Normally, however, users don't need to concern themselves with the contents of these files, as they can instead use utilities in the **Results of Hydration Simulation** submenu to plot any specific property of interest for the systems that have been hydrated.

References

[1] Number 04.02 in Annual Book of ASTM Standards. American Society for Testing and Materials, West Conshohocken, PA, 2000.

[2] D.P. Bentz. Cemhyd3d: A three-dimensional cement hydration and microstructural development modelling package. version 2.0. NISTIR 6485, U.S. Department of Commerce, April 2000.

[3] H. Bache, G.M. Idorn, P. Nepper-Christensen, and J. Nielsen. Morphology of calcium hydroxide in cement paste. In *Symposium on Structure of Portland Cement Paste and Concrete*, number 90 in HRB Special Report, pages 154–174. Highway Research Board, 1966.

[4] S. Diamond and J. Huang. The itz in concrete—a different view based on image analysis and sem observations. *Cement and Concrete Composites*, 23:179–188, 2001.

[5] H.F.W. Taylor. *Cement Chemistry*. Thomas Telford, London, second edition, 1997.